

PATENT SPECIFICATION

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(54) POLYETHYLENEIMINE DERIVATIVES

(71) We, ROHM AND HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention is concerned with condensation polymers of polyethyleneimine and one or more dihaloalkanes. The polymers of the invention are useful as anion exchange resins.

Certain condensation polymers of polyethyleneimine have been described in the prior art. However, many of these resins, prepared by heating a mixture of polyethyleneimine and a dihaloalkane tend to develop a very high rinse requirement when used in purifying water. Condensation polymers of polyethyleneimine and dihaloalkanes, having a high anion exchange capacity, wherein this tendency is less marked have now been found.

According to the invention, there is provided a process for the production of anion exchange resins which comprises (a) condensing at least one polyethyleneimine with at least one dihaloalkane, and then (b) reacting the resin product of (a) with alkylating agent, preferably a methylating agent, to convert nontertiary amine groups in the resin product of (a) to tertiary or quaternary amine groups. The polyethyleneimine used in preparing the resins of the invention can have any of a wide range of molecular weights, and almost any conveniently available polyethyleneimine or equivalent will be suitable. As used in the present specification and claims, the term "polyethyleneimine" includes polymers having the polyethyleneimine structure prepared by indirect means such as condensation polymers of polyethylene polyamines. Generally, the most useful polyethyleneimines will have an average molecular weight of 300 to 60,000, and preferably 600 to 5000.

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A wide variety of dihaloalkanes can be used in the process of the invention. Among the most useful dihaloalkanes are (C₁—C₆) dihaloalkanes, for example 1,2 - dichloroethane (ethylene dichloride), 1,2 - dichloropropane, 1,3 - dichloropropane, 1,2 - dichlorobutane, 1,3 - dichlorobutane, 1,4 - dichlorobutane, 1,4 - dichlorobutene, 1,6 - dichlorohexane, and the corresponding bromides and iodides. Also included among the most useful dihaloalkanes are dihaloalkanes, for example bis(chloromethyl) benzene. Mixtures of dihaloalkanes can also be used. A preferred dihaloalkane is ethylene dichloride.

The ratio of polyethyleneimine to dihaloalkane can be varied over a wide range, depending on the degree of crosslinking which is desired in the resin. An increase in the ratio of dihaloalkane to polyethyleneimine will usually provide an increase in the degree of crosslinking. Generally, 0.1 to 0.6 moles, and preferably 0.15 to 0.45 moles, of the dihaloalkane per equivalent ethyleneimine unit in the polyethyleneimine may be used in preparing the polymers of the invention.

Any of the conventional condensation polymerization processes known in the art can be used in the process of the invention. Generally, the polyethyleneimine may be dissolved in water and added to the dihaloalkane and a suspending agent dissolved in a suitable solvent, for example, a hydrocarbon or chlorinated hydrocarbon, which is inert to the condensation reaction. The reaction is generally carried out at a temperature of 70 to 140°C., and preferably 85 to 125°C. The reaction can be carried out at atmospheric pressure, or at superatmospheric pressure, of generally up to about 2 or 3 atmospheres. Under some conditions, running the reaction at superatmospheric pressures will advantageously increase the incorporation of the dihaloalkane and lower the number of secondary amine groups in the precursor resin.

While the condensation reaction can be carried out without the use of a catalyst, an organic or inorganic base, for example

sodium hydroxide, sodium carbonate, calcium hydroxide, sodium acetate or sodium phosphate may facilitate the reaction. When a catalyst is used, generally 0.125 to 1.0 moles per equivalent ethyleneimine unit is most efficient, although any quantity which gives the desired catalysis can be used. In a preferred process for making the resins of the invention, delayed addition of the catalyst is practiced.

After the condensation of polyethyleneimine and the dihaloalkane, the resin formed is reacted with an alkylating agent, preferably a methylating agent, to convert nontertiary amine groups in the precursor resin to amine groups which are tertiary or quaternary. Preferably all, or substantially all of the nontertiary groups are converted in this step. Two general types of alkylation reaction may conveniently be employed—exhaustive alkylation and reductive alkylation.

The reductive alkylation reaction which is preferred is the Leuckart reaction, in which the nontertiary amine groups are reacted with formaldehyde and formic acid to form the corresponding N-methyl tertiary amine group. While the reaction can be run on the isolated precursor resin itself, it is generally carried out on the precursor resin in the partial chloride form from which organic solvents have been removed, without prior isolation. The reaction is generally carried out at a temperature of 25 to 100°C., preferably 55 to 90°C.

Procedures for carrying out this kind of reaction are generally well-known in the art. In one useful procedure of the invention, formaldehyde is added to an aqueous slurry of the precursor resin, and, after allowing a sufficient reaction period for the formation of the formyl intermediate, generally 1/2 to 2 hours, formic acid is added to the reaction mixture. For the nontertiary amine groups, in the precursor resin to be substantially completely methylated, generally at least 2 moles of formaldehyde and formic acid will be necessary for each equivalent of secondary amine in the precursor resin. Any other reductive alkylation reaction for converting nontertiary amine groups to tertiary amine groups which will not significantly interfere with the anion exchange properties of the precursors resin can also be used.

Various exhaustive alkylation techniques which are generally well-known in the art, can be used in the process of the invention to convert the nontertiary amine groups in the precursor resin to tertiary and quaternary amine groups. A preferred technique is the reaction of the precursor resin with an exhaustive alkylating agent. Suitable alkylating agents include alkyl halides, for example methyl, ethyl or propyl chlorides, bromides, and iodides, alkyl sulfates, for example

sulfate, alkylene oxides, for example ethylene oxide and epichlorohydrin. In one useful procedure, the alkylating agent is added to an aqueous slurry of the precursor resin at a temperature of 20 to 125°C., optionally in the presence of a basic catalyst, for example sodium or potassium hydroxide, sodium carbonate, magnesium or calcium oxide, or an organic amine, for example pyridine. A suitable molar excess of the alkylating agent is used to ensure conversion of all amine groups to tertiary or quaternary groups. Other procedures for carrying out exhaustive alkylation reactions are well-known in the art.

Resins of the invention are useful as weak base anion exchange resins, and have good capacity and/or stability characteristics. They may be used particularly suitably for removing strong acids from various aqueous compositions. The resins formed by the exhaustive alkylation of the precursor resin will contact both tertiary and quaternary amine groups, and thus will possess both weak base and strong base anion exchange capacity.

Preferred methods of carrying out the process of the invention will now be described in the following examples which are given for the purposes of illustration only.

Examples 1 to 5 Preparation of Stage (a) Resin Example 1)

Into a 5-liter, 3 neck flask equipped with a condensor, thermometer, and paddle-type stirrer are charged 2067 grams of chlorobenzene, 623 grams of ethylene dichloride, and 15 ml of suspending agent (7% solution in chlorobenzene of the diester of polybutenylsuccinic acid and N - (2 - hydroxyethyl) - 2 - morpholinone). To the flask is then added a solution of 533.2 grams of polyethyleneimine having an average molecular weight of 1800 (PEI-18, commercially available from Dow Chemical Co.) in 990.2 grams of deionized water. The reaction mixture is heated with stirring to about 89°C. over a two-hour period, and held at that temperature for about 20 hours. After heating the reaction mixture at about 92 to 94°C. for one hour, chlorobenzene and unreacted ethylene dichloride are stripped, while adding water to the flask to maintain an appropriately constant volume. After solvent and unreacted starting material have been removed, 30 grams of gelling agent (Attagel 50) is added, the reaction mixture is cooled to about 50°C. 400 grams of 50% sodium hydroxide solution is added, and the reaction mixture held at about 50°C. for an hour. After cooling to room temperature, the reaction mixture is backwashed and regenerated to yield 2510 grams (wet) of 24.0% solid resin in the free base form.

Example 2)

To a mixture of 250 ml of *o* - dichlorobenzene, 100 grams, of 1,6 - dibromohexane, and 0.75 ml of suspending agent in a 1-liter flask are added 50 grams of polyethyleneimine (average molecular weight 1800) in 50 grams of deionized water. Following the procedure of Example 1, with heating overnight at about 85 to 95°C. The reaction yields 360 grams (wet) of resin after backwashing and regeneration.

Example 3)

Into a 5-liter stainless steel pressure reactor equipped with a thermometer, temperature control, heating mantle, addition funnel, and stainless steel paddle-type stirrer are charged 550 grams of ethylene dichloride, 1500 grams of chlorobenzene, and 22 ml of suspending agent. Over a period of about one hour is added with stirring 718 grams of 60% aqueous polyethyleneimine having an average molecular weight of 600 (PEI-6, commercially available from Dow Chemical Co.) while maintaining the temperature at about 25°C. The reaction mixture is heated to about 85°C. over a two-hour period, and allowed to remain at 85°C. for another 4 hours. After cooling the reaction mixture to about 70°C. 615 grams of 30% aqueous calcium hydroxide slurry is added. The reactor is then closed and heated to about 120°C. at a pressure of about 40 to 45 psi for 14 hours. The reaction mixture is cooled to 90°C. and the solvent and unreacted starting material are stripped off and replaced with water. After cooling to room temperature, the reaction mixture is backwashed and regenerated to give the wet resin in the free base form.

Example 4)

Into a 5-liter stainless steel pressure reactor equipped as in Example 3 are charged 550 grams of ethylene dichloride, 1500 grams of chlorobenzene, and 33 ml of suspending agent. Into the addition funnel are placed 430 grams of polyethyleneimine having an average molecular weight of 1800 (PEI-18, commercially available from Dow Chemical Co.) and 287 grams of deionized water and the temperature adjusted to about 30 to 40°C. The aqueous polyethyleneimine solution is then gradually added to the reactor over a period of about 1 hour while maintaining the temperature in the reactor at about 35°C. The temperature in the reactor is increased gradually to about 85°C. and allowed to remain at about 85°C. for another 5 hours. After cooling the reaction mixture to about 70°C., to it are added 185 grams of calcium hydroxide and 20 grams of 50% aqueous sodium hydroxide in 700 grams of deionized water. The reaction mixture is heated to about 120°C. over a 1-hour period

and held at 120°C. for about 5 hours. When the reaction mixture has cooled to 40°C., it is transferred to a 5-liter 3-necked glass flask and the chlorobenzene and unreacted ethylenedichloride are azeotropically distilled from the mixture over a temperature range of about 85 to 102°C. During the distillation, water is added to the flask to maintain an approximately constant volume in the flask. After the distillation is completed, 25 grams of gelling agent (Attagel 50) are added. Backwashing and regenerating the reaction mixture with 5% sodium hydroxide solution gives the wet resin in its free base form.

Example 5)

Following the procedure of Examples 1 to 4, anion exchange resins are prepared using polyethyleneimines having average molecular weights of 1200, 4000, 5000, and 60,000, and using as dihaloalkanes 1,3 - dichloropropane, 1,4 - dichlorobutene - 2, a mixture of ethylene dichloride and 1,4 - dichlorobutane, and 1,2 - dichloropropane.

Example 6)**Reductive Methylation of Stage (a) Resin**

This example shows one suitable technique for carrying out the reductive alkylation of the stage (a) polyethyleneimine-dihaloalkane resin.

Following the procedure of Example 4, the Stage (a) resin is prepared. After the gelling agent has been added, the temperature of the reaction mixture is adjusted to about 25°C. and to it is added 610 grams of 27% formaldehyde. The reaction mixture is allowed to equilibrate at about 25°C. for about an hour, and 430 grams of 90% formic acid is then added slowly over a 1/2-hour period. The flask is heated to 55°C. over a 1-hour period and after being held for 1 hour at 55°C. is heated to 75°C., held for 3 hours, heated to 90°C., and held for about 2 1/2 hours. After cooling to room temperature, the reaction mixture is charged to a backwash tower where it is backwashed and regenerated.

The reaction yields a stable weak base ion exchange resin (34.9% solids) having a total anion exchange capacity of 12.5 meq/g.

Example 7)**Exhaustive Methylation of Stage (a) Resin**

This example shows one suitable procedure for carrying out the exhaustive alkylation of the stage (a) polyethyleneimine-dihaloalkane resin.

To a 5-liter stainless steel pressure reactor at 25°C. are charged 100 grams of precursor resin (33.9% solids, prepared as in Example 4), 500 grams of deionized water, and 40 grams of sodium carbonate. The reactor is then pressurized to 50 psi with an excess molar amount of methyl chloride. After being

held at about 25°C. for 20 hours, the unreacted methyl chloride is removed and the reaction mixture is backwashed and regenerated to yield 114 grams (wet) of 54.5% solids resin in the free base form, having an 87.5% quaternization base on increase in weight. This resin shows both strong base and weak base anion exchange capacity.

When methyl bromide, methyl sulfate, ethyl chloride, and ethylene oxide are used as alkylating agents, similar exhaustive alkylated anion exchange resins are obtained.

WHAT WE CLAIM IS:—

1. A process for the production of ion exchange resin which comprises (a) condensing at least one polyethyleneimine with at least one dihaloalkane and then (b) reacting the resin product of (a) with alkylating agent to convert nontertiary amine groups in the resin product of (a) to tertiary or quaternary amine groups.

2. A process as claimed in claim 1 wherein the polyethyleneimine has an average molecular weight of 300 to 60,000.

3. A process as claimed in claim 1 or 2 wherein the polyethyleneimine has an average molecular weight of 600 to 5000.

4. A process as claimed in any preceding claim wherein (b) is carried out at a temperature of 25 to 100°C.

5. A process as claimed in any preceding claim wherein the dihaloalkane comprises (C₁—C₆) - dichloroalkane or (C₁—C₆) - dibromoalkane.

6. A process as claimed in claims 1 to 5 wherein the dihaloalkane comprises ethylene dichloride.

7. A process as claimed in any preceding claim wherein the alkylating agent comprises formaldehyde and formic acid.

8. A process as claimed in any of claims 1 to 6 wherein the alkylating agent is an alkyl halide.

9. A process as claimed in Claim 1 in which (a) is carried out substantially as described in any of Examples 1 to 5.

10. A process as claimed in Claim 1 in which (b) is carried out substantially as described in Example 6 or 7.

11. An ion exchange resin, the product of a process as claimed in Claim 1.

12. An ion exchange resin, the product of a process as claimed in any one of Claims 2 to 10.

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